# DIRECT WRITE PROCESSING FOR PHOTOVOLTAIC CELLS

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## ABSTRACT

Direct writing of solar cell components is an attractive processing approach. We have fabricated a 6.8% Si solar cell using silver ink based electrodes.  Ohmic contact through the antireflection (AR) coating was obtained with pure Ag electrodes at 850 $^0$C.  We also report on highly conductive silver metallizations and initial results on direct-write TCO demonstrating a 100-micron spatial resolution produced by inkjet printing.

## INTRODUCTION

A key issue in developing next generation photovoltaics is the ability to develop low cost production techniques and maintain or improve device quality.  Ink jet printing of metalorganic (MO) and nanoparticle based inks as precursors potentially offers the ability to deposit high quality electronic materials with the desired spatial resolution [1].  Versatility in the formulation of the liquid inks allows fine tuning of the compositions and control of doping levels of the materials produced so as to optimize the device performance.

We have previously demonstrated silver layers with conductivities near bulk that were spray-printed from solutions of MO precursors and from composite MO/nanoparticulate silver precursors [2].  Using composite precursors results in much greater deposition rates.  In both cases high adhesion strength to Si and to glass substrates was obtained without employing adhesion promoters such as glass frits or metallic adhesion layers.

For direct write contacts to be useful in photovoltaics applications they must form a low-resistance ohmic contact with the underlying semiconductor through any intervening layers. This requirement is especially challenging when the contact is fabricated on top of an antireflection coating such as the typically employed $Si_3N_4$[3].  In screen-printed contacts glass frits are incorporated in the Ag paste. These frits are believed to "burn" through the insulating layers at relatively low temperatures (~700 $^0$C) facilitating ohmic contact between Ag and Si [4].  Analogously, nanosized glass frits could be incorporated in the Ag inks for inkjet and spray printing.  In our initial experiments, however, we used pure MO-silver inks and studied the effect of high temperature annealing on contact resistance.  Here we report on inkjet and spray-printed silver contacts to Si solar cells with and without $Si_3N_4$ AR layers.

Transparent conducting oxides (TCO) represent another key solar cell component especially for thin film solar cells. These may also be amenable to direct write processing.  MO inks or colloidal nanoparticle suspensions can be developed based on known precursors for virtually all known TCO compounds.  Here we also report on initial results on the direct writing of transparent conducting oxides.  ZnO and $SnO_2$ were successfully printed from concentrated colloidal nanoparticulate precursors.  In addition, MO precursors containing both In and Sn sources were employed to directly deposit conducting ITO films.

## SPRAY-PRINTED CONTACTS TO Si

Silicon substrates with a diffused p-n junction, with and without a $Si_3N_4$ AR layer were provided by Evergreen Solar.  The substrates were briefly etched in 10% aqueous HF prior to Ag deposition.  MO (MO) silver inks were prepared by dissolving 2 mol (4.2g) of silver-(hexafluoroacetylacetonate)(1,5-cyclooctadiene) (Ag(hfa)COD) in 5 ml of toluene.  1$\mu$m thick Ag layers were spray-printed from the Ag-MO ink onto heated substrates at 400 $^0$C in air using a hand-held Vega 2000 airbrush. TLM grids (Figure 1) were patterned from the sprayed silver layer using photolithography and chemical etching in concentrated nitric acid.
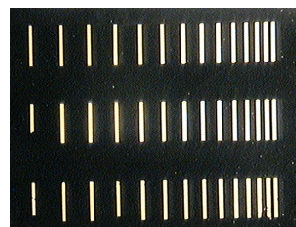


Figure 1. TLM pattern of Ag contacts fabricated on the n-type surface of Evergreen Solar material (the image is 2x).

For Si substrates without the AR coating, an ohmic contact with relatively low contact resistance of 0.4 m$\Omega$ cm$^2$ was formed immediately during Ag deposition.  For the substrates coated with silicon nitride, the $Si_3N_4$ dielectric layer electrically insulated the as-deposited silver contacts from Si and each other.

No current could be initiated between the contact pads by application of an external voltage up to 20 V, above which breakdown of the insulating layer was observed.

After the initial electrical testing, the samples containing AR coatings were annealed in a tube furnace in air at 600 $^0$C, 750 $^0$C, 800 $^0$C and 850 $^0$C for times ranging between 2 min and 1 hour.  Due to surface tension phenomena, the originally continuous Ag layers broke into islands in the course of firing (SEM Figure 2).  To form a continuous contact, another 2-micron thick layer of Ag was spray-printed on top of the already fired Ag pattern at 400°C and patterned using photoresist and etching, as before. Annealing at temperatures between 600 $^0$C and 800 $^0$C for a period of time from 2 minutes to 1 hour did not result in formation of ohmic contact, however the breakdown voltage for the annealed films was reduced to 1 V.
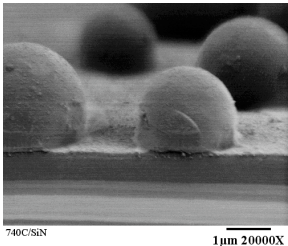


Figure 2. Ag layer breaks into isolated balls in the course of annealing at elevated temperatures

Ohmic contact between Ag and Si was obtained, however, in the samples annealed at 850 $^0$C for times as short as 5 minutes.  The best contact resistance achieved was 4 m$\Omega$ cm$^2$.  Following the contact resistance measurement, the Ag layer was removed by a prolonged etch in nitric acid, revealing the surface of the substrate under the contact.  The signs of the interaction between the substrate and Ag layer were evident by microscopic examination (Figure 3).
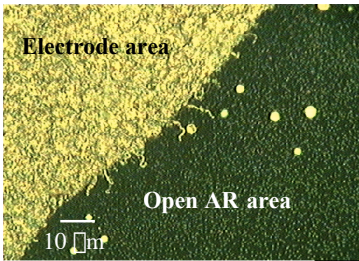


Figure 3. Optical micrograph of Ag printed on Si$_3$N$_4$-coated Si, annealed at 850°C and then etched, showing that the ink derived Ag burned through the AR coating.

An experimental 1cm$^2$ solar cell was prepared with spray-printed Ag contacts.  The Ag grids were fabricated in a similar fashion as the TLM patters described above (Figure 4). The back Al contact (1 $\mu$m thick) was deposited by e-beam evaporation after the first Ag grid was fabricated and prior to the high-temperature annealing step.  The front and the back contacts were co-fired at 850 $^0$C for ~ 10 minutes.
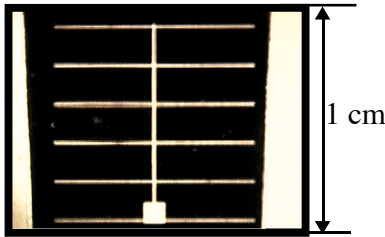


Figure 4. Si solar cell fabricated with spray-printed Ag burned through the silicon nitride layer

This resulted in simultaneous alloying and ohmic contact formation of the front and the back contacts with Si.  Again, the Ag layer broke into isolated islands in the course of the annealing.  A second Ag layer was spray-deposited and patterned over the original grid in order to provide continuous front contact.  The performance parameters of the fabricated cell are enumerated in the Table 1.

Table 1. The performance parameters of the cell with spray-printed front contacts.

| Voc | 0.5476 V |
|-----|----------|
| Jsc | 26.762 mA/cm$^2$ |
| FF | 46.16% |
| Eff | 6.76% |

The low fill factor (FF) is probably due to high series resistance resulting from insufficient thickness of the front and back contact metallizations.  This initial experiment demonstrates the feasibility of printed Ag contacts on Si solar cells and shows significantly that the metal-organic ink is capable of burning through the AR coating to form a low-resistance ohmic contact.

## INKJET-PRINTED SILVER ELECTRODES

The MO Ag inks were printed using a Microfab drop-on-demand inkjet printer.  In this system the drops are stimulated at the tip of a glass capillary by an acoustic wave produced by a piezoelectric actuator.  The frequency, and to some degree, the volume of the generated drops, can be controlled by an operator.  Such flexibility in printing parameters helps in controlling deposition rate and resolution of a printed line. When printing parameters are optimized, the most important factors that limit the line resolution are the size of the drop-generating

orifice and the wetting properties of the ink on the surface of a substrate.   Our MO Ag inks (Ag(hfa)COD in organic solvents) were printed on glass, Si and $Si_3N_4$ coated Si substrates using a 50 $\mu$m jet. The best line resolution (100 $\mu$m) (Figure 5) was achieved with butanol-based ink (highest viscosity solvent) printed on heated (120 $^0$C) glass substrates.



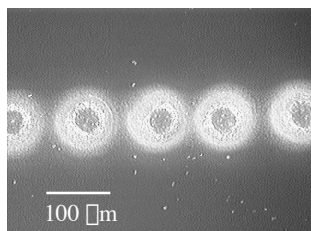Figure 5. Individual 100 $\mu$m Ag drops printed on glass at 120°C with the Microfab inkjet printer using Ag(hfa)(COD)/butanol ink.

The printed precursor lines turned into pure Ag during the following annealing step at 250 $^0$C in air.   The toluene-based inks demonstrate lower resolution but may be printed at temperatures above that required to decompose the precursor, thus directly producing Ag patterns without the need for postdeposition annealing (Figure 6).
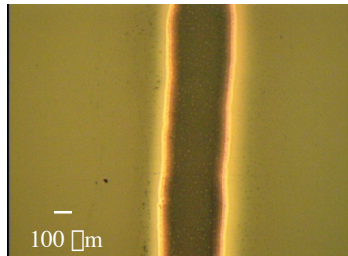


Figure 6. 300 $\mu$m wide Ag line printed on glass at 200 °C with the Microfab inkjet printer using Ag(hfa)(COD)/toluene ink.

The homogeneous MO inks are very compatible with the inkjet-printers.  High quality conducting lines are produced with MO inks, but the deposition rates are rather low (300Å - 500Å per pass). Thus we are developing alternate precursors that are capable of higher deposition rates.   Two approaches are currently being evaluated.  One is using alternate MO precursors capable of higher solubility in suitable solvents. Second is using concentrated suspensions of Ag nanoparticles.

Applying the former approach we have attained concentrations of up to 8M of Ag with a Ag-trifluoroacetate precursor in water.  This is four times higher concentration than that attained for (silver-(hexafluoroacetylacetonate)(1,5-

cyclooctadiene) and should lead to deposition rates up to 2000Å per pass.   The new concentrated ink was printable by inkjet and demonstrated pure silver deposits upon decomposition in air at 250 $^0$C.  Poor wetting of the substrate by the ink in our original printing experiments led to non-uniform distribution of the printed precursor making it difficult to evaluate the average thickness of the Ag deposit. Follow-on work will focus on optimizing ink rheological properties and the substrate surface to produce uniform layers.

Key to the latter approach is stabilizing concentrated Ag suspensions.  A certain degree of agglomeration would be tolerable, however aggregates with sizes greater than 5 microns would constrict the flow of the precursor through the orifice of the inkjet reducing line resolution and increasing the chance for clogging of the orifice of the inkjet.  Surface stabilization of the nanoparticles with organic surfactants may alleviate the agglomeration through stabilizing the suspension of the nanoparticles.  Developing stabilized nanoparticle inks has a potential to result in much greater deposition rates than the highest possible for MO precursors.  Initial results with composite nanoparticulate/MO precursors of Ag have shown that it is possible to attain up to 10 $\mu$m thick layers with conductivities within factor of two of that for bulk Ag.

### INKJET-PRINTED TCO

Water-based colloids of ZnO and $SnO_2$ from NYACOL were printed on Pyrex glass substrates at 125 $^0$C and 800 Hz deposition rate (800 drops per second).  Narrow (100 $\mu$m) and thick (5 $\mu$m) lines were printed in a single pass (Figure 7). As-printed pure ZnO and $SnO_2$ particulate precursors are not conductive.  Annealing in a reducing atmosphere as well as introducing doping elements (such as Al for ZnO and F for $SnO_2$) via intermixed MO compounds will be used to control the doping level in the printed oxides. In this approach, small amounts of water-soluble MO precursors are added to the colloidal suspension. The MOD reagent is uniformly dispersed in the colloid providing a uniform supply of doping elements.  When printed and annealed above the decomposition temperature of the MO precursor the dopant is free to diffuse into the oxide particles.  Also during the anneal the individual particles sinter together in a conducting continuum.   For nanoparticles this occurs at lower temperatures than normal because of surface energy considerations. Both reducing anneal and doping via MO will increase carrier concentrations and thus improve conductivity of the printed TCOs.

Conducting ITO films were also printed from a commercial (CHEMAT) MO ITO precursor in hexanes.  100 $\mu$m lines of the precursor were

printed at 50 - 75 $^0$C on Pyrex glass slides. Rectangular patterns of the precursor were produced by printing individual lines with 20-micron overlap.
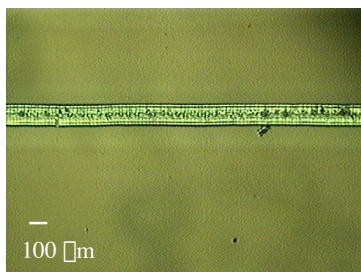


Figure 7. 100 $\mu$m SnO$_2$ line printed on glass at 125°C with the Microfab inkjet printer using NYACOL colloidal tin oxide precursor

The printed precursor patterns were decomposed by annealing in air at 300 $^0$C.  The solid and transparent 1000Å thick films thus produced had a resistivity of 300 Ohm cm.  Annealing in air at 700 $^0$C significantly improved the resistivity reducing it to 0.03 Ohm cm.  A further improvement in resistivity down to 0.004 Ohm cm was achieved with a one-hour reducing anneal in argon at 400 $^0$C.
With these initial experiments, we demonstrated that low resistivity transparent ITO patterns can be inkjet printed from MO precursors.  Also high deposition rates and good resolution were obtained for colloidal TCO precursors.

## SUMMARY

Metal contacts and transparent conducting oxide layers were printed from MO and nanoparticulate precursors.  High quality materials can be achieved by printing liquid precursors under atmospheric conditions.  Using direct write techniques such as inkjet printing may eliminate expensive steps of vacuum deposition, photolithography and etching, significantly reducing the cost of solar cell fabrication.  In addition, the ability to control the composition of the precursors in real time can lead to tremendous flexibility in controlling the conductivity and doping levels spatially.  Ink formulation and process optimization are underway to produce higher quality materials and more efficient devices by direct write techniques.

## REFERENCE

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